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ATTEMPTS TO INDUCE OPTICAL ACTIVITY WITH POLARIZED β-RADIATION

T. L. V. ULBRICHT[1] and F. VESTER
University Chemical Laboratory, Lensfield Road, Cambridge and Institut für Organische Chemie, Universität des Saarlandes, Saarbrücken, Germany[2]

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Abstract—The possible mechanisms whereby polarized β-radiation might induce optical activity during the course of chemical reactions are discussed qualitatively, and experiments to investigate such an effect in a variety of chemical systems are described. No unequivocal rotations (measured at the sodium D line) were obtained, and any induced optical activity was probably less than 0·02%.

THE discovery that parity is not conserved in weak interactions[3] revealed an intrinsic asymmetry in our part of the universe: the electrons emerging in β-decay are predominantly of one handedness. The two types of electrons are related by mirror-image symmetry which is, in principle, the same as that which gives rise to optical activity in chemical compounds.[3] It would be of great interest if a connection could be established between asymmetry at the level of elementary particles and at the molecular level, as this might relate the intrinsic asymmetry of matter (as distinct from anti-matter) with the asymmetry found in biological systems on this planet.[4,5] It is shown in this paper that the asymmetries can undoubtedly be related to each other theoretically, although this does not necessarily mean that a casual connection exists in nature.

A possible experimental approach to this problem is to attempt the induction of optical activity with polarized β-radiation. This has been discussed previously,[3,4] and preliminary results briefly reported.[6]

Irradiation of benzene with (necessarily symmetric) γ-rays from ^{60}Co is supposed to have produced a significant rotation,[7] but in a careful repetition of this experiment, no rotation was observed.[8]

Possible mechanisms of induction

1. *Bremsstrahlung.* It has been shown, theoretically and experimentally, that longitudinally polarized β-radiation gives rise to circularly polarized Bremsstrahlung, even at relatively low energies; the degree of asymmetry of the Bremsstrahlung is still 0·01 per cent for $h\nu = 100$eV.[6,9] Since circularly polarized light can produce

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[1] Present address: Twyford Laboratories Ltd., Twyford Abbey Road, London, N.W.10.

[2] Present address of F. V.

[3] T. L. V. Ulbricht, *Quart, Rev.* **13,** 48 (1959).

[4] F. Vester, *Seminar at Yale University, 7th February* (1957); *Habilitationsschrift* Saarbrücken (1962)

[5] T. L. V. Ulbricht, *The Optical Asymmetry of Metabolites* in *Comparative Biochemistry* vol. 4. (Edited by M. Florkin and H. Mason) Academic Press, New York, in press.

[6] F. Vester, T. L. V. Ulbricht and H. Krauch, *Naturwiss.* **46,** 68 (1959).

[7] S. V. Starodubtsev, M. N. Gurskij and A. G. Sizykh, *Doklady Akad. Nauk S.S.S. R.*, **129,** 307 (1959).

[8] L. Spialter and J. H. Futrell, *Nature, Lond.*, **188,** 225. (1960).

[9] K. W. McVoy, *Phys. Rev.* **106,** 828 (1957); **111,** 1484 (1958); M. Goldhaber, L. Grodzins and A. W. Sunyar, *Ibid.* **106,** 826 (1957); S. Galster and H. Schopper, *Nuclear Phys.* **6,** 125 (1958).

optical activity,[3] a route from polarized β-radiation to molecular asymmetry actually exists, but calculations show that, even assuming favourable circumstances, measurable optical activity would not be produced in any time reasonable for experimental investigation. (A source of 1 Curie, complete absorption of the β-radiation by the reactants, a product with a specific rotation of 100°, and a quantum yield of 1, might produce measurable optical activity in a period of the order of one year). However, in a reaction with a quantum yield considerably greater than 1—for example, a radiation-catalysed isotactic polymerization—measurable optical activity might be produced within the time of an ordinary chemical reaction.

2. *Magnetic effect.* Such an effect (orientation of spin-orbit interaction between the electrons) would be extremely small, because of the large differences between the energy levels of the β-ray and the molecular electrons. (Nothing would be gained by using radiation of low energy, since the degree of asymmetry of the β-rays is proportional to v/c, where v = velocity of β-ray, and c = velocity of light.)[3]

3. *Entropy exchange.* The reaction mixture together with the beam of radiation absorbed by it may be regarded as a closed system, in which entropy exchange takes place between two processes: (a) formation of product, and (b) absorption of radiation, such that the state of order of the molecules increases (i.e., optical activity is produced) while the state of order of the β-ray electrons decreases (depolarization). (Internal entropy exchanges of this kind are well known, for example, during crystallization from supersaturated solutions). Such an entropy effect during irradiation would have the same low order of magnitude as energetic interactions between β-ray electrons and molecules, i.e., comparable to 1 and 2.

4. *Non-energetic interaction.* Since optical isomers have the same scalar quantities and thus the same energy content, whether or not one of the two mirror-images is formed preferentially is a matter of probability (i.e., entropy). In the presence of longitudinally polarized (asymmetric) β-radiation (a state of order of low probability), the entropy, S, of the system expressed as

$$S = k \cdot \log_e P + \text{const.}$$

(where k is the Boltzmann constant, and P = probability) will be lower than that of a similar system with unpolarized electrons. If we disregard energetic interactions between relativistic electrons and molecules because of the large difference between their respective energy levels, a direct non-energetic interaction restricted to their asymmetry might still be possible. The order of magnitude of such an interaction between molecules and β-ray electrons would be independent of their energies (except in so far as the asymmetry of the β-rays depends on their initial energy).[3] What is required is a transmission of information regarding form, analogous to the exchange-"forces" of quantum physics. The Pauli Exclusion Principle, for example, introduces a correlation in the behaviour of particles which, though its effects are similar to the effects of forces, has no explanation in dynamic terms.[10]

5. *Other mechanisms.* In slowing down, the β-rays not only produce Bremsstrahlung, but also secondary electrons. It is not known whether these are polarized or not; if not, their effect would be to dilute that of any other mechanism operating. If the secondary electrons are polarized however, they could contribute to any overall effect.

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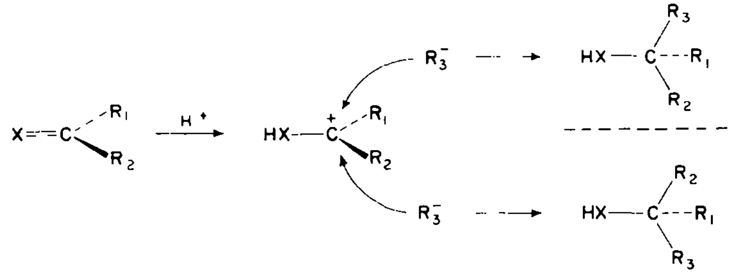
[10] H. Margenau, *The Nature of Physical Reality* McGraw-Hill, New York (1950).

Experimental conditions

Of the energetic interactions (1–3), the one proceeding via Bremsstrahlung has a sound theoretical and experimental basis, but in all of them the magnitude of the effect expected is small unless it be amplified in some manner; for example, by stereochemical propagation along a polymerizing chain, or by taking advantage of the Cotton Effect. (Circumstances unfortunately restricted the present investigation to optical measurements at the sodium D line). However, the experimental conditions, as far as the mechanism of the chemical reactions are concerned, would be less critical for one of these energetic interactions, than for a non-energetic mechanism. The latter requires a reactive intermediate in a state such that the formation of both optical isomers is equally possible, as in a reaction in which a planar sp^2 carbonium ion can give rise to either of the isomeric products, without energy being required to produce more of one form. Examples are acid and base-catalysed reactions in which a planar trigonal carbon atom is converted to a tetrahedral carbon atom with four different substituents, as in the generalized case:



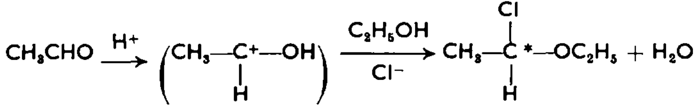
The magnitude of the effect will be proportional to the range of the β-rays and their asymmetry (given by $\frac{(R-L)}{(R+L)}$ where R and L are the fraction of right- and left-handed electrons, respectively), to the proportion of molecules along the track brought into a reactive state by the passing electron, and to the anisotropy of the product (if the rotation is to be measured at the sodium D line, then the magnitude will be proportional to the specific rotation); it will be inversely proportional to the minimum measurable rotation, the density of the reaction mixture and the diameter of the molecule containing the future asymmetric carbon atom. A preferred reaction would be carried out without solvent (higher impact probability) and yielding a liquid product (measurable without dilution), and should be one whose velocity is increased by the ionizing β-rays, so that it can be carried out at a temperature at which the uncatalysed reaction rate is negligibly small. For all types of interaction (1–4), a pure β-emitter without concommitant γ-decay would be a preferred source. Since the magnitude of some of the parameters involved in these interactions cannot be evaluated precisely, only experimental investigations can decide whether there is a measurable effect.

Reactions

(a) *Reactions involving carbonium ions.* It is not suggested that free carbonium ions are present in these reactions, but all of them involve reaction at an electrophilic carbon atom which becomes the new asymmetric centre, (C*).

With the exception of V, all these reactions were acid-catalysed.

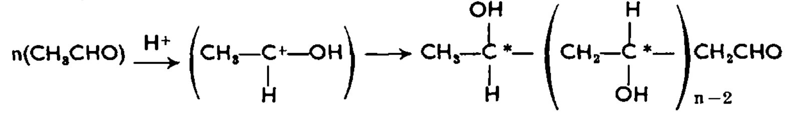
I. Synthesis of ethyl α-chloroethyl ether



$$CH_3CHO \xrightarrow{H^+} \left(CH_3-\underset{H}{C^+}-OH\right) \xrightarrow[Cl^-]{C_2H_5OH} CH_3-\overset{Cl}{\underset{H}{C}}{}^*-OC_2H_5 + H_2O$$

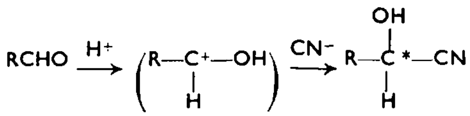
The mechanism had previously been studied using acetaldehyde-18.[11]

II. Aldol synthesis



$$n(CH_3CHO) \xrightarrow{H^+} \left(CH_3-\underset{H}{C^+}-OH\right) \longrightarrow CH_3-\overset{OH}{\underset{H}{C}}{}^*-\left(CH_2-\overset{H}{\underset{OH}{C}}{}^*-\right)_{n-2}CH_2CHO$$

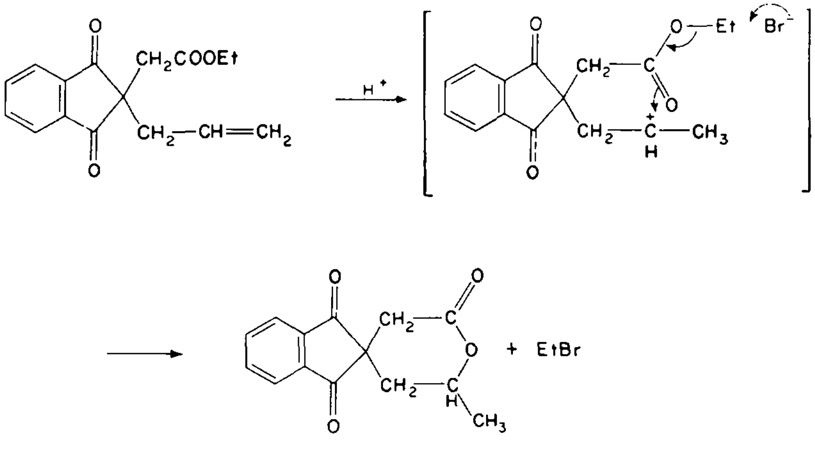
IIIA. Synthesis of mandelonitrile (R = Ph)



$$RCHO \xrightarrow{H^+} \left(R-\underset{H}{C^+}-OH\right) \xrightarrow{CN^-} R-\overset{OH}{\underset{H}{C}}{}^*-CN$$

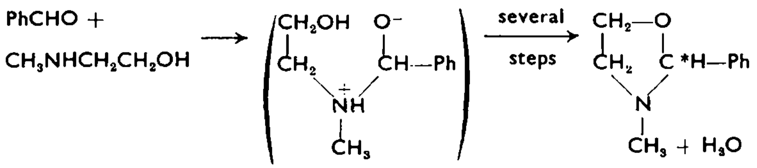
IIIB. Synthesis of lactonitrile (R = CH_3)

IV. Ring-closure to a spiro-compound:



This reaction had been used in a successful asymmetric synthesis using circularly polarized light.[12]

V. Synthesis of an oxazolidene:



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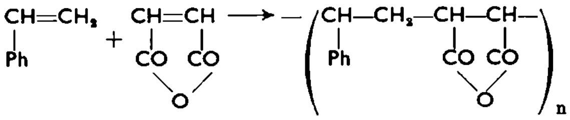
[11] H. Krauch and F. Vester, *Naturwiss.* **44**, 491 (1957).

[12] D. Radulescu and V. Moga, *Bul. Soc. Chim. Romania* **1**, 18 (1939).

(b) *A reaction involving free radicals*

VI. The copolymerization of styrene and maleic anhydride:



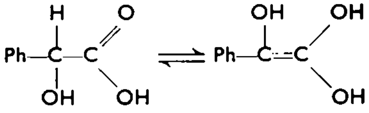
In this radical reaction, three different asymmetric carbon atoms are formed in each polymer unit, and no meso forms are possible. Analysis of the polymer showed that it was almost exactly a 1 : 1 copolymer.

(c) *Irradiation of racemic mixtures*

VII. D,L-Alanine was irradiated in the presence of metallic silver in a nuclear pile, and the short-lived isotopes ^{110}Ag and ^{108}Ag served as the sources. Depending on the conditions, considerable decomposition of the alanine took place; in these circumstances, more of one isomer might be destroyed than of the other, or an equilibrium in favour of one isomer established in the alanine not decomposed.

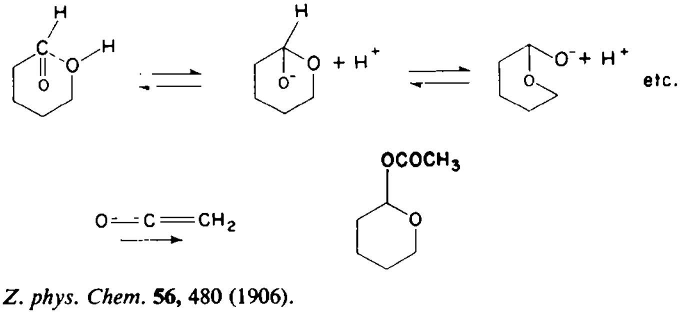
VIII. Irradiation of mandelonitrile in the presence of base. It was shown by Winther[13] that mandelic acid is rapidly racemized by alkali; the same would be expected to apply to the nitrile. After a short reaction time, acid was added to freeze the equilibrium between the isomers.

IX. Hydrolysis of mandelonitrile by acid. Erlenmayer[14] found that L-mandelic acid was completely racemized by heating an aqueous solution at 140° for two days. When the reaction was carried out with PhCHODCOOD in D_2O, no further hydrogen-exchange took place during racemization. Hence an enolic intermediate of the type



cannot be involved in racemization, as this would have led to a third deuterium atom being introduced. The present experiments were carried out at moderate temperatures in acid and one would not expect any change in configuration except in those molecules activated by irradiation.

X. 5-Hydroxypentan-1-al exists mainly in the cyclic form shown,[15] which undergoes constant mutarotation. By instantaneous reaction with anhydrous ketone during irradiation it was hoped to capture any transient excess of one optical isomer as the acetyl derivative:



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[13] C. Winther, *Z. phys. Chem.* **56**, 480 (1906).

Discussion

Control experiments with unpolarized electrons from a linear accelerator,[16] as well as the results obtained with a variety of radioactive sources, are listed in the Table. We noted, qualitatively, an acceleration of the reaction rate in all our irradiation experiments, which was very marked in all cases except Reaction 1. Some of the earlier experiments (4-8) with Reaction 1 appeared to give products with a small positive rotation. Repetition of these experiments and a careful polarimetric investigation by our colleague Dr. H. Krauch showed that, as already reported,[6] the results obtained were not significant. As no rotations were observed after the study of reaction I, control experiments were not carried out except in the case of VII (see Experimental).

Our results indicate that any optical activity produced by the sources available to us (relatively weak for this type of experiment) was very probably less than 0·02 per cent. This does not rule out the possibility that optical activity in nature may have arisen through one of the mechanisms discussed, over a very long period of time, but in a laboratory investigation a measurable effect could only be produced in a reasonable time by using stronger sources.

EXPERIMENTAL

Melting-points are uncorrected.

Apparatus. (A) The reaction chamber had a terylene (0·05 mm thickness) window, and was fitted with a fritted glass disc for the introduction of gases. (B) A spherical flask; the (protected) source was suspended in the centre of the reaction medium. (C) A thin (3 mm thickness) flat reaction vessel with terylene sides, placed on the source; the reaction mixture was passed through by means of a syringe. (D) A rounded inverted funnel, whose mouth was covered with terylene and placed on the source. (E) A glass conical flask with bottom thickness 0·2 mm, placed on the source.

In A, C, D and E the part of the apparatus serving as window was slightly larger in area than that of the source(s) used with it. Apparatus C had a capacity of 0·5 ml, the others of 2–3 ml. The apparatus used for a particular experiment is shown in the Table.

Sources. (1) ^{32}P, β^- 1·71 Mev, no γ, 100 mc, prepared from ^{32}S and condensed on aluminium foil (little back scattering) in the form of phosphoric acid. (2) ^{32}P, as (1), 1000 mC. (3) ^{90}Sr/Y, β^- 2·27 MeV, no γ, point source, 100 mC. (4) ^{90}Sr/Y, plaque source, 100 mC. (5) as (4), 500 mC. (6) ^{90}Y, capillary source, 30 mC. (7) ^{152}Eu, β^- 1·88 MeV, γ 0·34 MeV, capillary source, 2500 mC. (8) ^{108}Ag/^{110}Ag, β^- 1·77/2·87 MeV, γ 0·64/0·94 MeV; the short-lived isotopes were prepared in a nuclear pile in the course of the actual experiment.

To prepare the capillary sources, the inactive nuclide (^{151}Eu, ^{89}Y) was sealed in a small capillary tube (wall thickness, 0·2 mm), the tube wrapped in crushed aluminium foil to prevent mechanical shock, and subjected to bombardment in a nuclear reactor. The aluminium was removed by dissolving it in hydrochloric acid.

Ethyl α-chloroethyl ether (I) Acetaldehyde (1·0 ml) and absolute ethanol (1·0 ml) were introduced into the apparatus, cooled to −5° or to −20°, and dry hydrogen chloride passed into the reaction mixture from a generator stoichiometrically calibrated so as to deliver the required amount of gas (a slight excess) within a given period of time (5 min to 1 hr). After completion of the reaction, the product was removed with a syringe and immediately cooled to −70°. The organic phase was decanted from the lower, frozen aqueous phase, anhydrous magnesium sulphate added, the mixture placed in a vacuum desiccator, and vacuum gradually applied (water-pump) until no more bubbles formed. After removal of excess hydrogen chloride in this way, the pale straw-coloured liquid could

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[14] H. Erlenmayer, H. Schenkel and A. Epprecht, *Helv. Chem. Acta* **19,** 1053 (1936).

[15] L. E. Schniepp and H. H. Geller, *J. Amer. Chem. Soc.* **68,** 1646 (1946).

[16] Experiments carried out in the Linear Accelerator Laboratory at Yale University, by kind permission of Dr. H. L. Schultz.

be withdrawn by pipette and introduced directly into a polarimeter tube. In a control experiment with unpolarized electrons, it was found that 80% of the product was the desired ether (I).[11]

Aldol condensation (II). Acetaldehyde (2·0 ml) was treated with dry hydrogen chloride, and the product dried and degassed as above. It consisted of a mixture of aldols whose composition was not investigated. For reaction time, etc., see Table.

Mandelonitrile (IIIA). After introducing potassium cyanide (700 mg), benzaldehyde (1,0 g) and water (0·5 ml) into the apparatus, it was placed on the source, and fuming hydrochloric acid (1·0 ml) added immediately. The mixture was left on the source for 10 min., extracted with ether, dried over anhydrous magnesium sulphate, filtered, and the ether removed *in vacuo*. An infra-red spectrum showed that the product consisted predominantly of mandelonitrile, together with small amounts of benzaldehyde and mandelic acid.

Lactonitrile (IIIB). Excess gaseous hydrogen cyanide was introduced into the apparatus containing acetaldehyde (2·0 ml), and irradiated for 30 min. The rotation of the dried and degassed product (lactonitrile containing a trace of acetaldehyde) was determined immediately.

1,3-*Indanedione-2,2-spiro-1-methylpyran-5′-one* (IV) (a) To 2-allyl-2-methoxycarbonylmethylinda -1,3-dione (600 mg) in the apparatus on the source, hydrobromic acid (*d.* 1·8, 2·0 ml) was added, and left for 10 min at 50° or 12 hr at room temp. Hydrogen bromide was removed at 40°, water at 70°, *in vacuo*. Light petroleum (100–120°, 5 ml) was added and distilled, and the residue extracted with light petroleum (60–80°, 5 ml) which was discarded. The residue wss dissolved in benzene (10 ml), filtered, traces of water removed by distillation with a little absolute ethanol, and the product crystallized from benzene–light petroleum (80–100°) to give colourless prisms, 270 mg, m.p. 122–124° (lit[12] m.p. 121°). (b) The allylindandione (600 mg) and hydrogen bromide/glacial acetic acid (50% w/v, 2·0 ml) were left on the source for (i) 20 mins. at 50°; (ii) 100 min at 40°; (iii) 14 hr at room temp, and worked up as before, giving (i) 150, (ii) 285, and (iii) 340 mg of product, m.p. 122–124°.

The rotation of the spiran was measured as a 1:2 solution in chloroform.

3-*Methyl-2-phenyloxazobidene* (V). To N-methylethanolamine (1·36 ml) in the apparatus, benzaldehyde (1·64 ml) was added carefully by means of a pipette, so as to give two distinct layers, and left on the source for 12 hr. The product was homogeneous and coloured light yellow. Anhydrous sodium sulphate and ether were added, the solution centrifuged, and the supernatent distilled. The main, colourless fraction had b.p. 135°/14 mm (oil-bath temp) and 241°/251 mm (lit[17] b.p. 240°/246 mm).

Copolymerization of styrene and maleic anhydride (VI). Maleic anhydride (1·6 g) and styrene (freshly distilled in nitrogen under red press, 1·6 g) were introduced into the apparatus in an atmosphere of nitrogen, and the apparatus immersed in water at 45° to melt the anhydride and allow the agents to mix. The apparatus was then left on the source at 40°/50° for from 15 to 90 min. After removal of the terylene window, the pale yellow rubbery polymer was dissolved in the minimum volume of dimethyl formamide. Addition of methanol gave a colourless flocculent precipitate of the polymer, whose rotation was measured in dimethyl formamide solution. In blank experiments without irradiation, no reaction occurred under otherwise identical conditions. (Found, after drying at $140°/10^{-8}$: C, 71·1; H, 5·39. $(C_{12}H_{10}O_3)_n$ requires: C, 71·3; H, 4·98%).

Irradiation of D,L-*alanine* (VII). (i) and (ii) served as control experiments. All samples were left for 48 hrs. (i) D,L-Alanine (4·4 g) was surrounded by lead foil (1·4 g/cm^2) around which was wrapped inactive silver (11·2 g) and the whole inserted in an aluminium tube which was put in a nuclear pile for neutron bombardment. The β-rays were mostly absorbed by the lead. The decomposition of the alanine was estimated as 10–20% by dissolving the product in the minimum quantity of water, filtering and precipitating the alanine with ethanol. The identity of the alanine was checked by paper chromatography. (ii) As (i), but the alanine was surrounded by lead only. Decomposition was 0–10%, probably due to some γ-rays from the pile. (iii) No lead was used and the alanine (4·3 g) wrapped directly in silver (10·5 g) and aluminium foil. The decomposition was 70–80%. (iv) The alanine (4·45 g) was mixed directly with silver powder (10·8 g), stuffed down with aluminium foil and irradiated in the pile. The decomposition was nearly complete (96%). The reisolated alanine gave a yellow solution whose rotation was measured immediately. This showed a slight positive value, which may be due simply to the colour of the solution.[18]

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[17] L. Knorr and H. Matthes, *Ber. Dtsch. Chem. Ges.* **34**, 3486 (1901).

[18] A survey of possible errors in polarimetry is to be published by H. Krauch.

TABLE OF ROTATIONS

No.	Reaction	source	apparatus	Source geometry[a] (Steradians)	Irrad. time (mins.)	Temp. °C	Average rotation (standard dev.)
1	I	L.A.[b]	A	2	5	−5 to 0	+0·0005 ± 0·0077
2	I	L.A.[c]	A	2	5	−5 to 0	+0·0049 ± 0·0140
3	I	L.A.[d]	A	2	5	−5 to 0	+0·0068 ± 0·0053
4	I	1	A	1/3	5	−5 to 0	+0·012 ± 0·0042
5	I	1	A	1/3	60	−5 to 0	+0·0139 ± 0·0042
6	I	3	A	2	90	−20	+0·012 ± 0·0036
7	I	3	A	2	10	−5	+0·039 ± 0·0115
8	I	4	A	1/2	5	−5 to 0	+0·0215 ± 0·0074
9	I	4	A	1/2	5	−5 to 0	+0·0124 ± 0·0102
10	I	6	B	4	40	−20	+0·0088 ± 0·0071
11	I	6	B	4	6	−5	+0·0117 ± 0·0069
12	I	7	B	4	60	−20	+0·0013 ± 0·0039
13	I	7	B	4	60	−20	−0·002 ± 0·0138
14	II	6	B	4	600	−50 to −10	−0·026 ± 0·0092
15	II	7	B	4	600	−50 to −10	+0·0057 ± 0·0053
16	IIIA	5	E	2	10	+20	0·000 ± 0·012
17	IIIA	5	E	2	10	+20	+0·0095 ± 0·0157
18	IIIB	2	A	1/3	30	−10	+0·002 ± 0·008
19	IV	5	E	2	10	+50	−0·033 ± 0·072
20	IV	5	E	2	85	+50	−0·051 ± 0·035
21	IV	5	E	2	720	+20	−0·055 ± 0·033
22	IV	5	E	2	840	+20	—[e]
23	V	2	E	2	720	+20	−0·006 ± 0·005
24	VI	5	E	2	13	+50	−0·003 ± 0·010
25	VI	5	E	2	30	+50	+0·015 ± 0·027
26	VI	5	E	2	60	+50	+0·000 ± 0·009
27	VI	5	E	2	60	+20	—[e]
28	VI	5	E	2	90	+50	−0·002 ± 0·028
29	VI	5	E	2	500	+50	−0·052 ± 0·050
30	VII	8	—[f]	2	2900	—[f]	−0·005 ± 0·007
31	VII	8	—[f]	4	2900	—[f]	+0·016 ± 0·008
32	VIII	5	C	2	10	+50	−0·001 ± 0·012
33	VIII	5	C	2	540	+20	+0·003 ± 0·011
34	IX	5	E	2	200	+20	+0·013 ± 0·030
35	IX	5	E	2	720	+20	+0·010 ± 0·020
36	X	5	D	2	10	+20	+0·034 ± 0·020

[a] Estimated solid angle of radiation entering reaction chamber.

[b] Linear Accelerator, 5 impulses, each of 10^{10} electrons in 10^{-6} secs, max energy 6·5 MeV.

[c] As above, 80 impulses.

[d] As above 500 impulses.

[e] Not measurable—solution not sufficiently clear.

[f] See text.

Irradiation of mandelonitrile (VIII). To the nitrile (2·0 ml) in ethanol (1·0 ml) containing a drop of phenolthalein solution (0·5%), was added sodium hydroxide solution (0·05 N, 4 drops). The orange-coloured solution was left on the source for 10 min at 40°. Hydrochloric acid (0·2 N, 1 drop) was added, and the apparatus left on the source until the colour of the whole solution had changed back to yellow (4 min). Ether and a little water were added, and the mandelonitrile isolated in the usual way.

Hydrolysis of mandelonitrile (IX). The nitrile (1·5 ml) in the apparatus was placed on the source, and fuming hydrochloric acid (1·5 ml) added and left for 3 or 12 hr. Ether was added and filtered from the crystals which had separated. Removal of the ether gave an oil which consisted of benzaldehyde, mandelic acid and a little mandelonitrile; the crystalline product was pure mandelic acid, m.p. 118°.

5-*Acetoxypentan*-1-*al* (X). 5-Hydroxypentan-1-al was prepared from tetrahydrofurfuryl alcohol via dihydropyran, and its I.R. spectrum indicated that the compound existed mainly in its cyclic form, 2-hydroxy-tetrahydropyran, in accordance with previous findings.[15] It was purified by distillation at 63–66°/10 and stored in a sealed tube. The irradiation experiment was carried out by passing ketene (with trap at −35°) through the apparatus containing the pentanalol (2·0 ml) for 40 min at room temp. The product was distilled, giving a colourless liquid, b.p. 60°/5. The I.R. spectrum showed the presence of unchanged pentanalol (single-bridge hydrogen-bonded OH, 2·94; hydrogen-bonded carbonyl, 6·06) as well as product (ester, 5·78 μ).

Precautions against optical contamination. The reagents were checked in the polarimeter, and no rotation detected. During all the experimental procedures, reagents and products came into contact only with glass, terylene and polyethylene. Liquid transfer was carried out by pipette or syringe. No stopcock or other grease was used.

Polarimetry. Both instruments were visual, a Rudolph polarimeter direct reading 0·01°, and a Zeiss-Kreisspolarimeter, 1959 model, direct reading 0·01°, subdivisions by estimation. For each sample (including controls, and determination of the null-point) a minimum of 10 readings was taken, repeated by at least one observer, who had no knowledge of the identity of the sample. All readings were taken at the sodium D line. The standard deviation (sigma value) was calculated in the usual way:

$$\sigma = \sqrt{\frac{(\sigma_1)^2 + (\sigma_2)^2}{2}}, \qquad \sigma_{1,2} = \sqrt{\frac{\Sigma m_i^2}{n-1}}$$

where m_i are the deviations of each reading α_i from the mean,

$$\alpha_m = \frac{\Sigma \alpha_i}{n}$$

Our experience indicated that under ordinary conditions, readings of less than 0·05° obtained with a visual Lippich-halfshadow polarimeter, even with apparantly significant sigma values, may not be reliable.[18]

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